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Thienyl-containing β-Diketones: Synthesis, Characterization, Crystal Structure and Keto-enol Kinetics

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ABSTRACT

1-phenyl-3-(2-thenoyl)-1,3-propanedione, Hbth, $pK_a' = 9.006(8)$ and 1,3-di(2-thenoyl)-1,3-propanedione, Hdtm, $pK_a' = 8.893(3)$ were prepared by the Claisen condensation of ethyl 2-thiophenecarboxylate with an appropriate ketone under the influence of lithium diisopropylamide (LDA). The group electronegativity of the thienyl group is 2.10 (Gordy scale) as calculated from a linear group electronegativity *vs.* methyl ester IR carbonyl stretching wavenumber relationship. A crystal structure determination of Hbth (orthorhombic, Pbca, $Z = 8$, $R = 0.0290$) shows asymmetrical enolization on the side of the phenyl group. The preferred enol isomer of β-diketones containing more than one aromatic moiety that crystallizes in the solid state is determined by the resonance driving force stabilization of the thienyl or any other aromatic group, rather than the stabilization by resonance due to the phenyl group. The slow conversion of the enol isomers to the keto-enol equilibrium position was followed in $CDCl_3$ solution by NMR spectroscopy.

KEYWORDS

β-Diketone, thienyl, crystal structure, keto-enol tautomerism, resonance.

1. Introduction

Enols and enolate ions are critical intermediates in many important reactions.[1] The determination of keto-enol equilibrium constants and the effect of the pH on the UV absorption spectra of *β*-diketones by techniques such as bromine titration,[2] exchange with deuterium,[3] polarographic measurements,[4] energy of enolization,[5] UV,[6] IR[7] and NMR spectroscopy[8] have been at the centre of physical organic studies for many years.[9]

β-Diketones exist in solution in three tautomeric forms, as illustrated in Scheme 1, for the thienyl-containing *β*-diketones. Open chain 1,3-dicarbonyl compounds are observed in the *trans*-enolic form (not shown) only in rare cases.[10] In solution, *β*-diketones enolize predominantly to the *cis*-enolic form which is stabilized by intramolecular hydrogen bonding. In a symmetrically substituted *β*-diketone, e.g. acetylacetone, there is only one indistinguishable enolic form: the two valence bond structures that may be written for the *cis*-enolic form contribute equally to the total structure of the enol. On the other hand, when the *β*-diketone is unsymmetrically substituted, e.g. benzoylacetone, two enolic structures with unsymmetrical hydrogen bonds may exist, in which the fractions of the two types of isomers present at equilibrium depend on the nature of the substituents and possibly on the medium in which the compound is located. The interconversion between both enol isomers involves merely an intramolecular proton transfer (proven by NMR studies in a non-polar solvent) with a concomitant change in the electron distribution of the molecule. The rate of this transfer is fast, even on the nuclear magnetic resonance time scale, and consequently the peaks in the NMR spectra of the two enolic forms are a weighted average. In the case of benzoylacetone, it was spectroscopically indicated that enolization is predominantly in a direction away from the aromatic phenyl group in $CDCl_3$ solution.[16]

Separate ^{1}H NMR resonance signals are always observed for the protons of the various groups in the keto and enol tautomers of *β*-diketones. The equilibrium between the keto and enol forms of the *β*-diketones can be expressed in terms of the equilibrium constant K_c (Scheme 1). The keto-enol interconversion of *β*-diketones is generally a fast reaction.[11] Slow keto-enol conversion kinetics for a series of ferrocene-containing *β*-diketones, both in the solid state and in solution, explains why freshly prepared *β*-diketones contain higher percentages of the keto tautomer.[12] The research reported in the current paper on the isomerization of 1,3-di(2-thenoyl)-1,3-propanedione (Hdtm **1**) and 1-phenyl-3-(2-thenoyl)-1,3-propanedione (Hbth **2**), shows that, conversely to what was found for 1,1,1-trifluoro-2,4-pentanedione (Htta **3**),[13] the rate of conversion of the enol to the keto tautomer is a slow reaction. Acid dissociation constants and the temperature dependence of the keto–enol equilibrium constant are also presented.

Two different driving forces that may determine the preferred enol isomer of *β*-diketones in solution were postulated by du Plessis *et al.*[14] (see Fig. 1). The first driving force, labelled an

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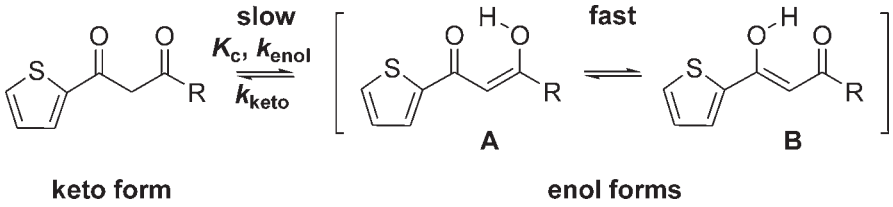

Scheme 1 Keto-enol equilibrium for thienyl-containing *β*-diketones.

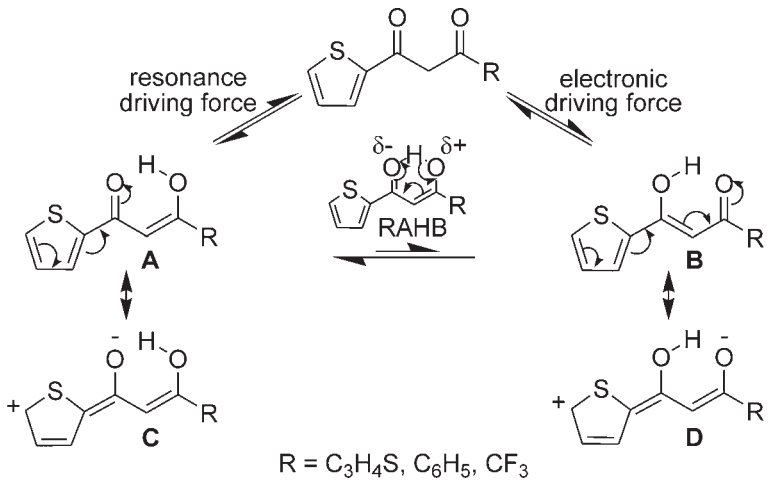

Figure 1 Resonance and electronic driving force influences on the preferred enol isomer of β-diketones in solution.

electronic driving force, implies that the group electronegativity, χ_R, of the substituents R and R′ on the β-diketone $RCOCH_2COR'$ will determine which enol isomer will be favoured. Regarding Htta **3**, with R = thienyl (Th, $\chi_{Th} = 2.10$)[15] and R′ = CF_3 ($\chi_{CF3} = 3.01$),[16] the carbon atom of the carbonyl group adjacent to the thienyl group will be less positive in character than the carbon atom of the other carbonyl group. Consequently, from an electronic point of view, the dominant enol isomer should be $ThC(OH)=CHCOCF_3$ (**B** in Fig. 1). This was not found to be the case in the solid state.[17]

The second driving force, the resonance driving force, has priority over the electronic driving force when either or both the substituents R and R′ are an aromatic group such as ferrocenyl or phenyl, to determine which enol isomer will be favoured.[12,16] Resonance stabilization (long-distance electronic forces) would favour the formation of intermediates such as **A** and **C** while short distance electronic forces favour the formation of intermediates resembling **B** and **D** in Fig 1. The resonance driving force implies that the formation of the different canonical forms of a specific enol isomer will lower the energy of this isomer (such as **C**) sufficiently to allow its dominance over the existence of the other isomers (such as **D**) which may be favoured by electronic effects. Indirect evidence for the canonical forms comes from the crystal structure determination of the enol form of various ferrocene-containing β-diketones.[12,14,16]

Electronic considerations in terms of electronegativity, χ ($\chi_{CF3} = 3.10$, $\chi_{methyl} = 2.34$, $\chi_{thienyl} = 2.10$), favour **B** as the enol form of Hbth **2** and Htta **3**. However, structure A was shown by crystallography to be dominant, implying that the equilibrium between **A** and **B** lies far to the left. A relatively small dihedral angle of 5.88 ° for Hbth **2** and 0.83–1.67 ° for Htta **3** between the aromatic thienyl group and the pseudo-aromatic β-diketone core implies that the energy-lowering canonical form **C** makes a noticeable contribution to the overall existence of Hbth **2** and Htta **3**. A synergistic interplay of resonance and hydrogen bond (HB) formation, called resonance-assisted hydrogen bonding (RAHB), stabilizes the two enol forms **A** and **B** of the β-diketone.

There is a need to demonstrate that the resonance driving force arguments[16] are also valid for thienyl-containing β-diketones, $ThCOCH_2COR$, where R is an aromatic group such as Ph or when R has a considerably larger group electronegativity than the thienyl group, such as CF_3. Since charge delocalization from the enol plane in β-diketones into an aromatic side group is a function of the dihedral angle between the aromatic ring and the enol plane, steric factors forcing the aromatic ring out of the plane of delocalization could also determine the preferred enol isomer in β-diketones containing one or two aromatic groups. A crystal structure determination of an enol isomer of a β-diketone containing two aromatic groups is presented in this study.

In the solid state it is observed that for phenyl-containing β-diketones, enolization in certain cases involves the aromatic phenyl group and in others it does not.[18] In this paper the dominant isomeric enol stabilized by the resonance driving force in β-diketones containing more than one aromatic moiety, e.g. thienyl and phenyl, is investigated.

2. Experimental

2.1. Materials and Apparatus

Solid reagents and the β-diketone Htta **3** (Merck, Aldrich and Sigma) were used without further purification. Liquid reactants and solvents were distilled prior to use. Water was doubly distilled. CH_3CN was dried over CaH_2 and freshly distilled prior to use.

2.2. Synthesis

2-Acetylthiophene was prepared *via* acylation according to a published procedure.[19] Both **1** and **2** were synthesized under rigorous Schlenk conditions as follows. The system was flame-dried and degassed with Ar for 30 min. An Ar atmosphere was maintained during the reaction. 10.00 mmol of the appropriate ketone (1.2618 g 2-acetylthiophene for **1** or 1.2260 g acetophenone for **2**) was mixed with THF (1.0 cm^3) and stirred for a few minutes. Lithium diisopropylamide, LDA, (5.60 cm^3 of a 1.8 mol dm^{-3} solution in hexane, 10.0 mmol) was added while stirring and kept cool on an ice-bath. The transparent brown solution was allowed to stir a further 15 min at 0 °C. 95 % ethyl 2-thiophenecarboxylate (1.6442 g, 10.00 mmol) was added and the reaction mixture was allowed to stir for 12 h at room temperature resulting in a milky solution. The precipitate was filtered off, acidified with HCl (50 cm^3, 0.3 mol dm^{-3}) and immediately extracted with diethyl ether (3 × 50 cm^3). The combined extracts were thoroughly washed with water, dried ($MgSO_4$) and the solvent was removed under reduced pressure. Recrystallization from diethyl ether gave spectroscopically pure **1** (18.5 %) and **2** (18.8 %).

Characterization data for Hdtm **1**: m.p. 76.6–78.4 °C; δ_H/ppm (600 MHz, $CDCl_3$) 4.49 (2H, s, keto CH_2), 6.56 (1H, s, enol CH), 7.17 (2H, dd, $^3J = 5$ Hz, $^3J = 4$ Hz, keto CH), 7.18 (2H, dd, $^3J = 5$ Hz, $^3J = 4$ Hz, enol CH), 7.63 (2H, dd, $^3J = 5$ Hz, $^4J = 1$ Hz, enol CH), 7.72 (2H, dd, $^3J = 5$ Hz, $^4J = 1$ Hz, keto CH), 7.79 (2H, dd, $^3J = 4$ Hz, $^4J = 1$ Hz, enol CH), 7.91 (1H, dd, $^3J = 4$ Hz, $^4J = 1$ Hz, keto CH);

(Found: C, 55.8; H, 3.2 %. Calc. for $C_{11}H_8S_2O_2$ (236.31); C, 55.9; H, 3.4 %).

Characterization data for Hbth **2**: m.p. 74.0–76.7 °C; δ_H/ppm (600 MHz, $CDCl_3$) 4.57 (2H, s, keto CH_2), 6.71 (1H, s, enol CH), 7.17 (1H, dd, ^3J = 5 Hz, ^3J = 4 Hz, keto CH), 7.19 (1H, dd, ^3J = 5 Hz, ^3J = 4 Hz, enol CH), 7.51 (2H, m, keto + enol CH), 7.59 (1H, m, keto + enol CH), 7.66 (1H, dd, ^3J = 5 Hz, ^4J = 1 Hz, enol CH), 7.71 (1H, dd, ^3J = 5 Hz, ^4J = 1 Hz, keto CH), 7.83 (1H, dd, ^3J = 4 Hz, ^4J = 1 Hz, enol CH), 7.86 (1H, dd, ^3J = 4 Hz, ^4J = 1 Hz, keto CH), 7.97 (2H, m, enol CH), 8.06 (2H, m, keto CH); (Found C, 67.8; H, 4.3 %. Calc. for $C_{13}H_{10}SO_2$ (230.29); C, 67.8; H, 4.4 %).

2.3. Spectroscopy and Calculation of Percentage Keto Isomer and K_c Value

^{1}H NMR spectra of thienyl-containing β-diketones (0.012 mol dm^{-3} in $CDCl_3$) were recorded at 298 K on a Bruker Avance II 600 NMR spectrometer [^{1}H (600.130 MHz)]. The chemical shifts were reported relative to $SiMe_4$ (0.00 ppm). Integration of spectra was done in such a way that the methine proton, Th-CO-C**H**=C(OH)-R at *ca.* δ 6.47–6.71 ppm was always assigned an integral value of one. Appropriate NMR signals, mostly the CH_2/CH keto-enol signal pair of the pseudo-aromatic β-diketone core, were identified and the percentage keto tautomer was calculated using:

$$\% \text{ keto tautomer} = [(I \text{ of keto signal})/\{(I \text{ of keto signal}) + (I \text{ of enol signal})\}] \times 100\ \% \quad (1)$$

with I = integral value. Once the percentage keto tautomer was known, the equilibrium constant, $K_c = k_{enol}/k_{keto}$, applicable to Scheme 1, was obtained from:

$$K_c = (\% \text{ enol tautomer})/(\% \text{ keto tautomer}) = (100 - \% \text{ keto tautomer})/(\% \text{ keto tautomer}) \quad (2)$$

with K_c = equilibrium constant, k_{enol} = rate constant for the conversion of keto to enol tautomer and k_{keto} = rate constant for the conversion of enol to keto tautomer.

2.4. Calculation of Thermodynamic Quantities

The numerical values for the changes in the thermodynamic quantities reaction Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the equilibrium reaction written as in Scheme 1, were calculated from the formulae $\Delta G = -RT \ln K_c$, $\ln K_c = -\Delta H/RT$ + constant and $\Delta G = \Delta H - T\Delta S$,[20] assuming that the activities may be replaced by concentrations. This is a perfectly valid assumption under the experimental conditions, since it is known that ionic solutions at low concentrations approach ideal behaviour, implying that under these experimental conditions concentrations and activities are equal.[21]

2.5. Kinetics

We have found that directly after isolation of the β-diketone from a basic aqueous solution during the synthesis procedure, the keto form is present in appreciable quantities for all the synthesized β-diketones. This, however, does not represent the solution or solid state equilibrium keto–enol position for these compounds. It was found that the solution equilibrium position for all β-diketones is not the same as the solid state equilibrium position. In the solid state, during a slow kinetic process the keto isomer is converted to the enol isomer. Consequently, after enough time has elapsed, in the solid state, the equilibrium applicable to Scheme 1 is essentially driven completely to the enol side. Therefore, upon dissolving matured samples of Hdtm **1** and Hbth **2** in $CDCl_3$, the keto content of the $CDCl_3$ β-diketone solution was for all practical purposes zero and the slow formation of the keto tautomer until the solution keto–enol equilibrium position was reached, could be monitored. For a reversible first-order reaction of the type

$$\text{enol} \underset{k_{enol}}{\overset{k_{keto}}{\rightleftharpoons}} \text{keto}$$

the integrated concentration-time equation is given by[22]

$$[A]_t = [A]_{eq} + ([A]_0 - [A]_i)\exp^{(-k_{obs})t} \quad (3)$$

with $[A]_t$ = % keto isomer at time t, $[A]_{eq}$ = % keto tautomer at equilibrium, $[A]_0$ = initial % keto tautomer, $k_{obs} = k_{keto} + k_{enol}$. For each time interval the percentage keto tautomer was determined and the observed first-order rate constant, k_{obs}, was obtained from (3) utilizing the fitting program MINSQ.[23] The individual rate constants k_{keto} and k_{enol} were obtained by simultaneously solving the equations $k_{obs} = k_{keto} + k_{enol}$ and $K_c = k_{enol}/k_{keto}$ (Scheme 1).

2.6. Acid Dissociation Constant (K_a) Determinations

The pK_a values were determined by measuring the absorbance of 0.07 mmol dm^{-3} β-diketone solutions at different pHs during an acid-base titration in acetonitrile:water mixtures, 1:9 by volume, μ = 0.100 mol dm^{-3} ($NaClO_4$) at 25.0(5) °C as described earlier.[16]

2.7. X-ray Crystal Structure Determination for 1-Phenyl-3-(2-thenoyl)-1,3-propanedione, Hbth 2

A light brown regular crystal was used for the X-ray crystallographic analysis of compound **2** (Table 3). The initial unit cell and data collection were achieved by the Apex2 software[24] utilizing COSMO[25] for optimum collection of more than a hemisphere of reciprocal space. The intensity data were collected on a Bruker X8 Apex II 4K Kappa CCD diffractometer using an exposure time of 10 s per frame. A total of 1128 frames were collected with a frame width of 0.5 ° covering up to θ = 28.32 ° with 99.7 % completeness accomplished. The frames were integrated using a narrow-frame integration algorithm and reduced with the Bruker SAINT-Plus[26] and XPREP software packages, respectively. Data were corrected for absorption effects using the multi-scan technique SADABS.[27] The structure was solved by the direct methods package SIR97[28] and refined using the WinGX software package[29] incorporating SHELXL.[30] The molecular plot was drawn using the DIAMOND program[31] with a 50 % thermal envelope probability for non-hydrogen atoms.

3. Results and Discussion

3.1. Synthesis of Complexes

The β-diketones Hdtm **1** and Hbth **2** were prepared in yields not exceeding 19 % by the Claisen condensation of the appropriate ketone with ethyl 2-thiophenecarboxylate (an ester) in the presence of the base LDA. Pure products were obtained after acidification with dilute HCl and extraction with diethyl ether from the reaction mixture. In chloroform solutions the enol form of all the β-diketones dominates. Although the chemical shift data clearly show that the majority of the equilibrium is enolic, it is not possible to indicate the dominant structure of the enol in solution, which can be either **A** or **B** in Scheme 1.

3.2. Keto-enol Equilibrium in β-Diketones

From a ^{1}H NMR study, by comparing the relative intensities of suitable keto-enol signal pairs as described in the experimental section, the percentage of the enolized tautomers in $CDCl_3$

Table 1 Equilibrium and kinetic constants (in $CDCl_3$ at 25 °C) for the keto-enol equilibrium of thienyl-containing β-diketones and the thermodynamic quantities relevant to this equilibrium.

β-Diketone	K_c [a]	% keto	χ_R	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1} [b]	ΔS/J K^{-1} mol^{-1}	k_{enol}/s^{-1}	k_{keto}/s^{-1}
Hdtm **1**	4.5	18.0	2.10	–7.0	–3.7	–11	1.4×10^{-4}	3.1×10^{-5}
Hbth **2**	12.9	7.2	2.21	–9.1	–6.3	–9	3.3×10^{-5}	2.6×10^{-6}
Htta **3**	16.8	5.6	3.01	–8.0	–7.0	–3	[c]	[c]

[a] [β-diketone] = 0.0012 mol dm^{-3}.
[b] At 25 °C.
[c] Too fast to measure.

solution at 25 °C of the thienyl-containing β-diketones Hdtm **1**, Hbth **2** and Htta **3** was established (Table 1). The bottom NMR spectrum in Fig. 2, for example, demonstrates that at equilibrium, 18.0 % of the dissolved Hdtm **1** exists in the keto form and the remaining 82.0 % represents the enol isomer of Hdtm **1**. An increasing tendency towards enolization for the thienyl-containing β-diketones is observed as the electronegativity of the side group on the β-diketone, χ_R, increases from Th (χ_R = 2.10)[15] to Ph (χ_R = 2.21)[16] to CF_3 (χ_R = 3.01).[16]

Results of a temperature-dependent ^{1}H NMR study of the keto-enol equilibrium of the thienyl-containing β-diketones are summarized in Table 1 and illustrated in Fig. 3. The enol content of all three β-diketones generally decreases as the temperature is increased, due to the disruption of hydrogen bonds.[32] A 50 °C increase in temperature resulted in an increase of the percentage keto tautomer of approximately 80 %, 50 % and 70 % for Hdtm **1**, Hbth **2** and Htta **3**, respectively. As ΔG becomes more negative, in other words the thermodynamic driving force associated with Scheme 1 becomes more favourable, the keto content of the β-diketones decreases. The small negative ΔS value obtained for the conversion from keto to enol structures (Scheme 1) implies a lowering in the degree of disorder of the β-diketone molecules in changing from keto to enol.

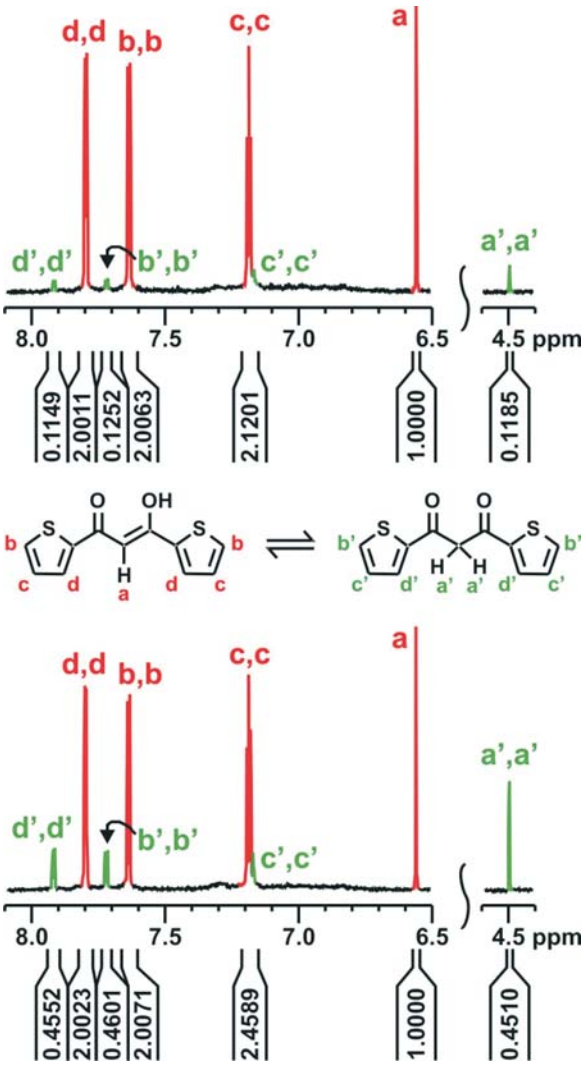

Figure 2 Top spectrum: ^{1}H NMR spectrum of Hdtm **1** that was allowed to reach keto-enol equilibrium in the solid state, recorded as fast as possible after the sample dissolved. Bottom spectrum: ^{1}H NMR spectrum of Hdtm **1** at equilibrium in $CDCl_3$ at 25 °C. The assignment of the peaks is indicated in the structures. The $CDCl_3$ peak is suppressed for clarity.

3.3. Kinetics of Ketonization

Figure 2 (top) illustrates the enol-enriched and the equilibrium ^{1}H NMR spectrum of Hdtm **1** in $CDCl_3$ solution. The conversion of the enol to the keto tautomer was monitored by recording ^{1}H NMR spectra at 25 °C at specific time intervals until equilibrium in solution was reached (Fig. 4). The first-order rate constant (k_{obs}) was found to be 0.00017(2) s^{-1} for Hdtm **1**, 0.000036(2) s^{-1} for Hbth **2** and to be too fast to measure for Htta **3**, consistent with the finding of Iglesias.[1] From these data the rate constants for the forward reaction (k_{enol}) and the reverse reaction (k_{keto}) in Scheme 1 were calculated and are given in Table 1. Larger rate constants for the conversion of keto to enol (k_{enol}) were observed compared with the conversion of enol to keto (k_{keto}) for both β-diketones in this study. This implies that the enol isomers are the favoured stable tautomer in which Hdtm **1**, Hbth **2** and Htta **3** exist in $CDCl_3$ solutions. For Htta **3** the equilibrium in $CDCl_3$ sets in within seconds, whereas for Hdtm **1** the

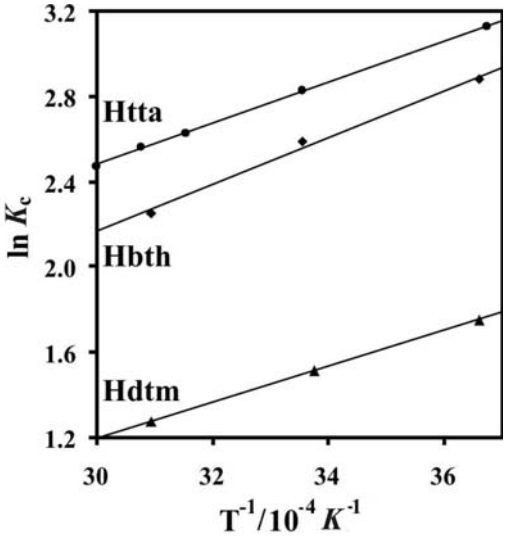

Figure 3 Temperature dependence of K_c for the equilibrium position between the keto and enol tautomers of the β-diketones Hdtm **1**, Hbth **2** and Htta **3**. Slope of graph = –ΔH/R.

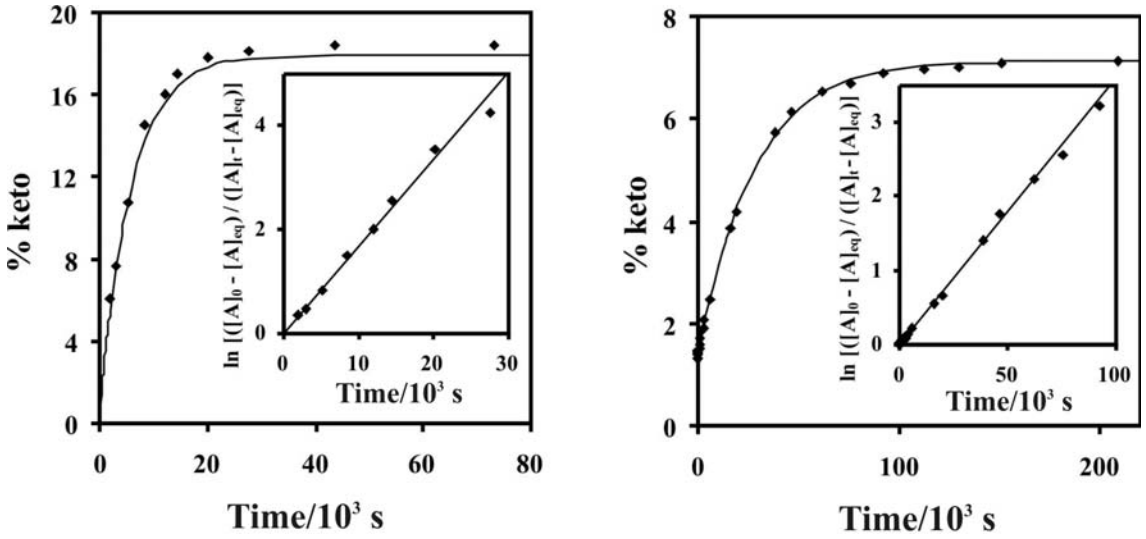

Figure 4 Time traces showing the conversion from the enol to the keto isomers of Hdtm **1** (left) and Hbth **2** (right) at 25 °C in $CDCl_3$. Inset: a kinetic plot of the data led to the observed first-order rate constants. [A] = % keto tautomer.

equilibrium was reached only after 15 h and Hbth **2** after 62 h. The thienyl-containing β-diketones Hdtm **1** and Hbth **2** have relatively slow equilibrium kinetics with k_{enol} ten to a hundred times faster than those measured for a series of ferrocene-containing β-diketones.[12]

3.4. Determinations of the Acid Dissociation Constant (K_a') and Group Electronegativity of the Thienyl Group, C_4H_3S

The pK_a values obtained for the conjugated keto-enol system of the different thienyl-containing β-diketones are tabulated in Table 2. The values obtained fit the general trend that the β-diketone becomes more acidic as the electronegativity of the side groups on the β-diketone increases, see Fig. 5. The pK_a' of Htta **3**, determined as 6.491(8) in this study, is within 1–4 % of the published pK_a' values of 6.23 in 1950[33,34] (determined by the direct titration with sodium hydroxide of an aqueous ketone solution at room temperature), 6.38 in 1952[34,35] and 6.53 in 1962.[34,36]

It has previously been shown that accurate apparent group electronegativities, χ_R, of the R group for esters of the type R(C=O)(OCH_3) can be obtained from a linear fit between χ_R and the IR carbonyl stretching wavenumber.[16,47] The straight line generated by the fit of χ_R and $\bar{\nu}$ (C=O) (Fig. 6) fits the equation $\bar{\nu}$ (C=O)$_R$ = 74.53 χ_R + 1561 and was used to determine the effective or apparent group electronegativity of the thienyl group (R = C_4H_3S) as 2.10 on the Gordy scale.

Table 2 pK_a' values and molar absorptivities (ε) at λ_{max} of the β-diketones Hdtm (**1**), Hbth (**2**) and Htta (**3**) in a 10 % acetonitrile:water mixture, μ = 0.100 mol dm^{-3} $NaClO_4$ at 25.0(5) °C.

β-Diketone[a]	pK_a'	λ_{max}(deprotonated)/nm	ε/dm^3 mol^{-1} cm^{-1}
Hdtm **1**	8.893(3)	382	17498
Hbth **2**	9.006(8)	365	23039
Htta **3**	6.491(8)	340	17720

[a] [β-diketone] = 0.07 mol dm^{-3}.

3.5. *X*-ray Structure of Hbth 2

A molecular diagram of Hbth **2** showing atom labelling is presented in Fig. 7. Crystal data for the structure of Hbth **2** are

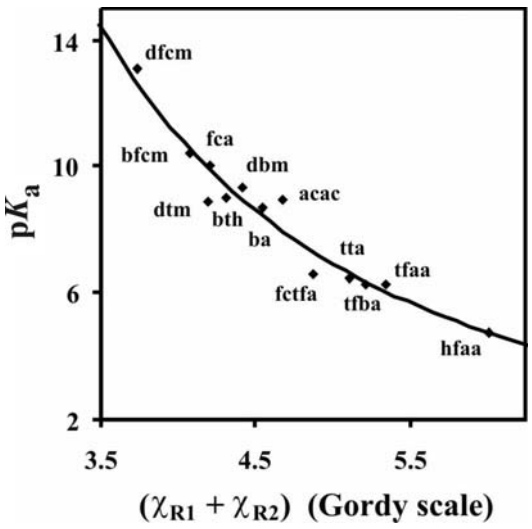

Figure 5 Relationship between the pK_a values and the sum of the group electronegativities (χ_{R1} + χ_{R2}) of the groups R^1 and R^2 of the β-diketone $R^1COCH_2COR^2$. pK_a values from references 14, 34, 45, 46 and this study.

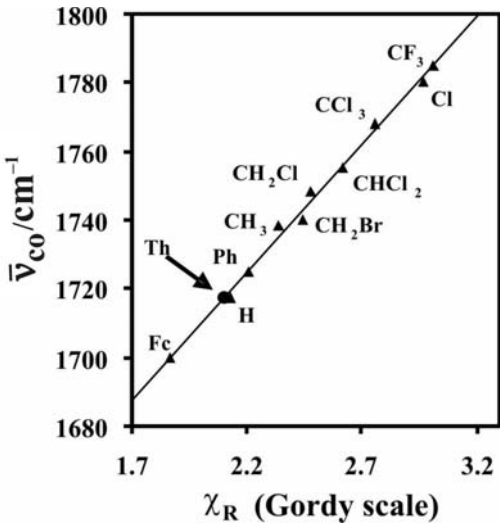

Figure 6 Linear relationship between the carbonyl stretching wavenumbers ($\bar{\nu}_{CO}$) and Gordy scale group electronegativities (χ_R) of the R groups of the esters of the type $RCOOCH_3$. Calibration data from references 16 and 47 allowed the determination of χ_{Th} from $\bar{\nu}$(C=O)$_R$ = 1717 cm^{-1} for $ThCOOCH_3$.

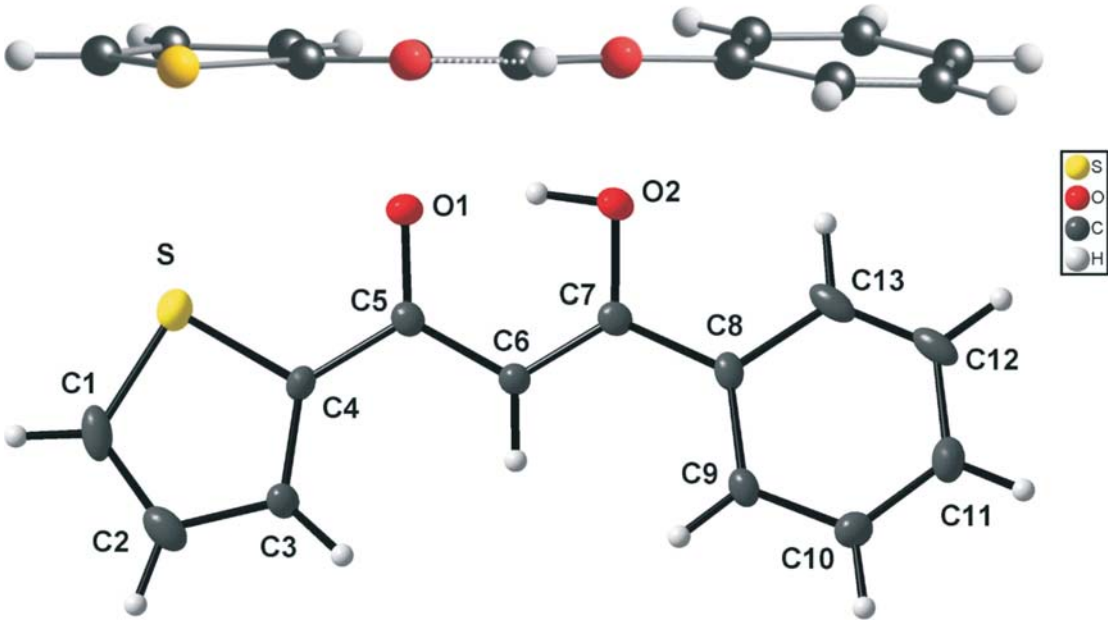

Figure 7 Bottom: Molecular diagram of 1-phenyl-3-(2-thenoyl)-1,3-propanedione (Hbth **2**) showing atom numbering and displacement ellipsoids with a 50 % probability. Top: side view of Hbth **2**, with the plane of the enol ring perpendicular to the page, showing the non-planar arrangement.

summarized in Table 3, and selected bond lengths, angles and torsion angles can be found in Table 4. The β-diketone Hbth **2** packs in the *Pbca* space group with $Z = 8$, resulting in the molecules lying in the general positions of the unit cell. All bond lengths and angles are in the typical ranges for these types of compounds.[18,37]

The molecule as a whole is non-planar (Fig. 7 top), possibly due to crystal packing, as several close contacts are observed in Mercury.[38] The planes of the phenyl ring and the thienyl ring make angles of 13.65 ° and 5.88 °, respectively, with the plane of the enol ring. When comparing the geometrical data of the three thienyl-containing β-diketones of this paper, the striking difference is that Hbth **2** is non-planar, while both Hdtm **1** and Htta **3** can be considered as planar, since the angle between the plane of the thienyl ring(s) and the plane of the enol ring are 0.85–4.92 ° for Hdtm **1** and 0.83–1.67 ° for Htta **3**, see Table 5. The bond

Table 3 Crystal data and structure refinement for Hbth **2**.

Empirical formula	$C_{13}H_{10}O_2S$	F(000)	960
Formula mass	230.27 g mol^{-1}	Crystal size	0.35 × 0.24 × 0.12 mm^3
Temperature	100(2) K	Theta range for data collection	2.95 to 28.32 °
Wavelength	0.71073 Å	Index ranges	–11 ≤ h ≤ 11
			–14 ≤ k ≤ 14
			–31 ≤ l ≤ 31
Crystal system	Orthorhombic	Reflections collected	21300
Space group	*Pbac*	Independent reflections	2695 [R(int) = 0.0290]
Unit cell dimensions	a = 8.4329(2) Å	Completeness to theta = 28.35 °	99.7 %
	b = 10.6891(2) Å	Maximum and minimum transmission	0.9674 and 0.9089
	c = 24.0104(5) Å	Refinement method	Full-matrix least-squares on F^2
	α = 90 °	Data/restraints/parameters	2695/0/143
	β = 90 °	Goodness-of-fit on F^2	1.063
	γ = 90 °	Final R indices [I > 2 sigma(I)]	R1 = 0.0634, wR2 = 0.1705
Volume	2164.30(8) Å^3	R indices (all data)	R1 = 0.0698, wR2 = 0.1768
Z	8	Highest peak	1.35 e Å^{-3} (0.45 Å from C13)
Density (calculated)	1.413 g cm^{-3}	Deepest hole	–0.82 e Å^{-3} (0.19 Å from C12)
Absorption coefficient	0.278 mm^{-1}		

Table 4 Selected bond lengths, angles and torsion angles for Hbth **2**.

Bond lengths/Å					
S-C4	1.721(2)	O2-H14	0.94(4)	C5-C6	1.435(3)
O1-C5	1.268(3)	C1-S	1.693(3)	C6-C7	1.371(3)
O2-C7	1.330(3)	C4-C5	1.457(3)	C7-C8	1.469(3)
Bond angles/degree					
C1-S-C4	91.85(12)	O1-C5-C4	118.9(2)	O2-C7-C8	114.47(19)
C3-C4-C5	128.6(2)	C6-C5-C4	119.9(2)	C6-C7-C8	124.6(2)
Torsion angles/degree					
S-C4-C5-O1	3.3(3)	C5-C6-C7-O2	-0.5(3)	O2-C7-C8-C13	–12.5(3)

Table 5 Selected geometrical data of the thienyl-containing β-diketones Hdtm **1**, Hbth **2** and Htta **3**.

β-Diketone	Enol type [a]	C=O bond length /Å	C-O (enol) bond length /Å	C=C bond length between carbonyl groups /Å	C-C bond length between carbonyl groups /Å	Angle between carbonyl (C5-C6-C7) groups /degree	O....O distance /Å	Space group	Angle between planes through thienyl group and enol group /degree
Hdtm **1**[39] [b]	asym enol	1.286(2)	1.308(2)	1.38(6)	1.41(3)	118.3(2)	2.514	*Cc*	0.85, 3.59
	sym enol	1.278(2)	1.283(2)	1.40(3)	1.41(3)	120.0(2)	2.517		0.85, 4.92
Hbth **2**	asym enol	1.268(3)	1.330(3)	1.371(3)	1.435(3)	119.9(2)	2.477	*Pbca*	5.88
Htta **3**[17] [b]	asym enol	1.269(4)	1.306(4)	1.343(4)	1.432(5)	120.4(3)	2.522	$P2_1/n$	0.83
	asym enol	1.272(4)	1.310(4)	1.353(5)	1.417(4)	120.8(3)	2.511		1.67

[a] In asymmetric enolization the ring hydrogen is bound much more tightly to one oxygen atom than to the other.
[b] Two molecules in the same asymmetric unit.

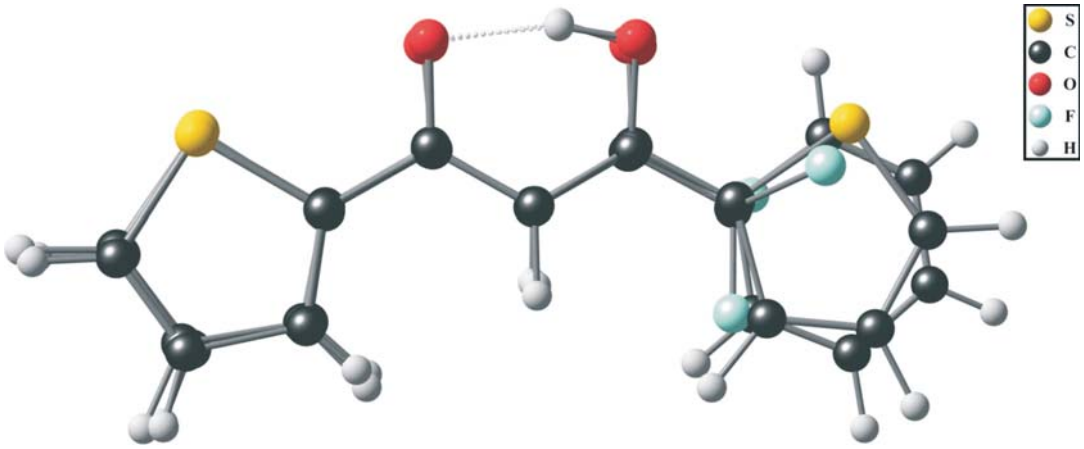

Figure 8 Superimposed view of the three thienyl-containing β-diketones Hdtm **1**, Hbth **2** and Htta **3**.

lengths and bond angles in the backbone of the β-diketone are all similar for Hdtm **1**, Hbth **2** and Htta **3**, as can be seen from the tabulated bond lengths and angles in Table 5 and the superimposed view of Hdtm **1**, Hbth **2** and Htta **3** in Fig. 8.

Figure 9 shows the packing of the molecules in the unit cell having a 'herring bone' arrangement. The molecules are stacked with the propanedione moieties in opposing directions, *i.e.* in a 'tail to tail' fashion. π-Stacking arrangements with interplanar distances of *ca.* 4.038 Å are observed between opposing phenyl and thienyl substituents. The 'herring bone' arrangement was also observed for Hdtm **1**.

In the structural analysis, the bond lengths indicate that a dominant enol tautomer is formed and that a tautomeric equilibrium between the two enol forms in the solid state is not

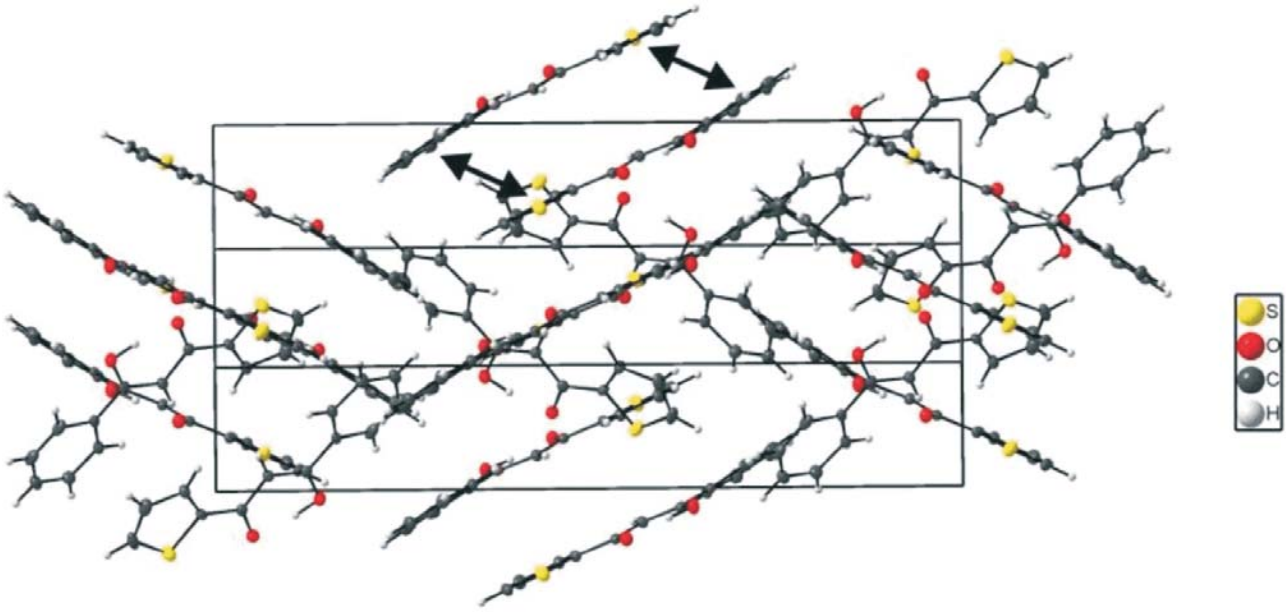

Figure 9 Packing diagram of Hbth **2** molecules in unit cell. Note the 'herring bone' arrangement of the molecules and the π-stacking of Hbth **2** molecules.

predominant: C7-O2 is longer than C5=O1 and C6=C7 is shorter than C5-C6 (Table 4). In all the thienyl-containing β-diketones **1**–**3** the thienyl S atom(s) is *cis* to the O atoms of the central enol moiety, possibly due to the S…O interactions between neighbouring molecules, also observed from a packing diagram in Mercury.

The electronegativity (χ_R) of a Ph group is slightly higher than that of a Th moiety (2.21[16] and 2.10[15], respectively). According to the electronic driving force, the hydroxyl proton should thus be located on the side of the Th. However, the hydroxyl proton is located on the opposite side. A possible reason for this could be that although both the Ph and the Th groups are aromatic, the larger angle observed between the Ph and enol planes compared with the angle between the planes of the Th and enol moieties implies that the conjugation between the pseudo-aromatic enol ring and the thienyl ring is stronger. Thus, the resonance driving force between the enol and the thienyl ring dominates over the electronic driving force, resulting in the hydroxyl proton being located on the side of the Ph group in Hbth **2**. Similarly, in the crystal structure of Htta **3**, the hydroxyl proton was also located on the side of the Th group as a result of the resonance driving force rather than the inductive electronic effect of the CF_3 group.

A theoretical bond angle value of 120 ° is expected for carbon sp^2 hybridization. The angle C5-C6-C7 (119.9(2)°) is within experimental error as expected.

Typical enolized β-diketone bond lengths are 1.269–1.283 Å and 1.306–1.337 Å for C=O and C-O bonds, respectively.[40] The bonds C5=O1 (Fig. 7) and C7-O2 are 1.268(3) Å and 1.330(3) Å, respectively and are in agreement with these typical bond lengths. The C5=O1 bond therefore displays double bond character and the C7-O2 bond displays single bond character. Normal C=C double bond lengths are typically 1.337 Å, while typical single C-C bonds have a length of 1.54 Å.[41] In β-diketones, however, these bonds are 1.343–1.392 Å and 1.403–1.432 Å, respectively.[40] These bonds are represented by C6-C7 (1.371(3) Å) and by C5-C6 (1.435(3) Å), which are in agreement with these typical bond lengths. The O…O distances for an enol and a keto β-diketone vary between 2.40–2.54 Å[42,43] and 2.77–3.3 Å[42,43], respectively. The O1…O2 distance of 2.477 Å is thus typically that of an enolized β-diketone. From a difference map, the hydroxyl H is shown to be approximately 0.615 Å farther away from O1 than from O2 with O2-H *ca.* 0.942 Å. Hbth **2** can thus be classified as an asymmetrical enol, since the ring hydrogen is bonded more tightly to the O2 atom.

4. The Resonance Driving Force

Crystallographic data may be used as support for the existence of the resonance driving force on the assumption that the enol that crystallizes from solution is the dominant and more stable enol in solution. Crystallographic data of thienyl-containing β-diketones indicated enolization in the direction farthest from the thienyl group.[18] Similarly, crystallographic data of ferrocene-containing β-diketones indicated enolization in the direction farthest from the ferrocene group.[18] NMR spectroscopy indicates that enolization in a direction farthest from the ferrocenyl group dominates in solution. However, crystallographic data of phenyl-containing β-diketones include enols with enolization adjacent to, as well as away from the phenyl group.[18] Careful examination of the crystallographic data of the two enol forms of phenyl-containing β-diketones Ph-C(OH)=CH-CO-R or Ph-CO-CH=C(OH)-R, indicates the following:[44]

1. If R = ferrocenyl or thienyl or any aromatic group, then asymmetrical enolization is adjacent to the phenyl group.
2. If R = non aromatic group, then asymmetrical enolization is adjacent to the R group (consistent with what was found for benzoylacetone in $CDCl_3$ solution).[16]
3. Symmetrical enolization occurs in rare cases.

Thus, in β-diketones containing more that one aromatic moiety, the resonance driving force stabilization of the ferrocenyl, the thienyl or the other aromatic group will take preference over the stabilization by resonance due to the phenyl group in favour of Ph-C(OH)=CH-CO-Ar (Ar = aromatic moiety). The resonance driving force leads to the formation of mainly the specified enol isomer in solution, consistent with the isomer that crystallizes in the solid state.

5. Conclusions

Asymmetrical enolization in the direction farthest from the thienyl group, adjacent to the phenyl group was observed for 1-phenyl-3-(2-thenoyl)-1,3-propanedione in the solid state. This finding is considered to be the result of resonance driving forces rather than inductive electronic effects of substituents on the pseudo-aromatic β-diketone core. In β-diketones containing more that one aromatic moiety the resonance driving force due to any aromatic group other that phenyl will take preference over the resonance driving force due to the phenyl group in determining which asymmetrical enol isomer will predominate in solution and consequently crystallize in the solid state.

6. Supplementary Data

Supporting information: X-ray crystallographic files in CIF format for Hbth **2**. Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre; CCDC No. 640949. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.com.ac.uk or www.ccdc.cam.ac.uk). A summary of the crystal structures of phenyl-, thienyl- and ferrocenyl-containing β-diketones is provided in the supplementary data.

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References and Notes

1 E. Iglesias, *J. Org. Chem.,* 2003, **68**, 2680–2688.
2 K.H. Meyer, *Ann. Physik,* 1911, **380**, 212–220.
3 L.E. Marchi, *Inorg. Synth.,* 1926, **2**, 10–14.
4 G.G. Semerano and A. Chisini, *Gazz. Chim. Ital.,* 1936, **66**, 504–507.
5 J.B. Conant and A.F. Thompson, Jr., *J. Am. Chem. Soc.,* 1932, **54**, 4039–4047.
6 R.J. Irving and M.A.V. Ribeiro da Silva, *J. Chem. Soc., Dalton Trans.,* 1975, 798–800.
7 J. Powling and H. Bernstein, *J. Am. Chem. Soc.,* 1951, **73**, 4353–4356.
8 L.W. Reeves, *Can. J. Chem.,* 1957, **35**, 1351–1365.
9 (a) J.L. Burdett and M.T. Rodgers, *J. Am. Chem. Soc.,* 1962, **86**, 2105–2109; (b) D.J. Sardella, D.H. Heinert and B.L. Shapiro, *J. Org. Chem.,* 1969, **34**, 2817–2821; (c) M.M. Folkendt, B.E. Weiss-Lopez, J.P. Chauvel, Jr. and N.S. True, *J. Phys. Chem.,* 1985, **89**, 3347–3352; (d) E. Iglesias, *J. Phys. Chem.,* 1996, **100**, 12592–12599.
10 M. Moriyasu, A. Kato and Y. Hashimoto, *J. Chem. Soc., Perkin Trans.,* 1986, **2**, 515–520.
11 E. Iglesias, *Langmuir,* 2000, **16**, 8348–8446.
12 W.C. du Plessis, W.L. Davis, S.J. Cronje and J.C. Swarts, *Inorg. Chim. Acta.,* 2001, **314**, 97–104.
13 E. Iglesias, *Langmuir,* 2001, **17**, 6871–6880.

14 W.C. du Plessis, J.C. Erasmus, G.J. Lamprecht, J. Conradie, T.S. Cameron, M.A.S. Aquino and J.C. Swarts, *Can. J. Chem.,* 1999, **77**, 378–386.

15 See section 3.4 of this paper for the determination of the group electronegativity of the thienyl group.

16 W.C du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.,* 1998, 2507–2514.

17 R.D.G. Jones, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.,* 1976, **B32**, 1224–1227.

18 Cambridge Structural Database (CSD), Version 5.27, August 2006 update.

19 H.D. Hartough and A.I. Kosak, *J. Am. Chem. Soc.,* 1947, **69**, 1012–1013.

20 K.J. Laidler, J.H. Meiser and B.C. Sanctuary, *Physical Chemistry,* 4th edn., Houghton Mifflin Company, New York, USA, 2003, pp. 124, 151, 169.

21 P.W. Atkins, *Physical Chemistry,* 5th edn., Oxford University Press, Oxford, UK, 1994, p. 319.

22 J.H. Espenson, *Chemical Kinetics and Reaction Mechanisms,* 2nd edn., McGraw-Hill, New York, USA, 1995, pp. 46–49.

23 MINSQ, Least Squares Parameter Estimation, Version 3.12, 1990, MicroMath.

24 Apex2, Version 1.0-27, 2005, Bruker AXS Inc., Madison, Wisconsin, USA.

25 COSMO, Version 1.48, 2003, Bruker AXS Inc., Madison, Wisconsin, USA.

26 SAINT-Plus, Version 7.12 (including XPREP), 2004, Bruker AXS Inc., Madison, Wisconsin, USA.

27 SADABS, Version 2004/1, 1998, Bruker AXS Inc., Madison, Wisconsin, USA.

28 A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.,* 1999, **32**, 115–119.

29 L.J. Farrugia, WinGX Version 1.70.01, *J. Appl. Cryst.,* 1999, **32**, 837–838.

30 G.M. Sheldrick, SHELXL97 Program for Crystal Structure Refinement, 1997, University of Göttingen, Göttingen, Germany.

31 K. Brandenburg and H. Putz, DIAMOND, Release 3.1a. Crystal Impact GbR, 2005, Bonn, Germany.

32 B. Floris and J. Toullec, *The Chemistry of Enols* (Z. Rappoport, ed.), John Wiley & Sons, Chichester, UK, 1990, pp. 270, 361.

33 J.C. Reid and M. Calvin, *J. Am. Chem. Soc.,* 1950, **72**, 2948–2952.

34 J. Starý, *The Solvent Extraction of Metal Chelates,* MacMillan Company, New York, USA, 1964, Appendix.

35 E.H. Cook and R.W. Taft, *J. Am. Chem. Soc.,* 1952, **74**, 6103–6104.

36 V.M. Peshkova and Pen-An, *Zh. Neorg. Khim.,* 1962, **7**, 1484–1487.

37 F.H. Allen, *Acta Cryst.,* 2002, **B58**, 380–388.

38 Mercury 1.5, The Cambridge Crystallographic Data Centre, Cambridge, UK.

39 L.A.M. Baxter, A.J. Blake, G.A. Heath and T.A. Stephenson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 1990, **46**, 508–510.

40 W. Bell, J.A. Crayston, C. Glidewell, M.A. Mazid and M.B. Hursthouse, *J. Organomet. Chem.,* 1992, **434**, 115–121.

41 R.C. Weast, *Handbook of Chemistry and Physics,* 63rd edn., The Chemical Rubber Co., Cleveland, Ohio, USA, pp. F180–181.

42 S. Yamabe, N. Tsuchida and K. Kiyajima, *J. Phys. Chem., A,* 2004, **108**, 2750–2757.

43 A.H. Lowrey, C. George, P. D'Antonio and J. Karle, *J. Am. Chem. Soc.,* 1971, **93**, 6399–6403.

44 See Table A1 in the supplementary data for a summary of the crystal structures of phenyl-, thienyl- and ferrocenyl-containing β-diketones.

45 M. Ellinger, H. Duschner and K. Starke, *J. Inorg. Nucl. Chem.,* 1978, **40**, 1063–1067.

46 S.S. Basson, J.G. Leipoldt and J.T. Nel, *Inorg. Chim. Acta,* 1984, **84**, 167–172.

47 R.E. Kagarise, *J. Am. Chem. Soc.,* 1955, **77**, 1377–1379.